Chapter 13

Making an Earth

Thus God knows the world, because He conceived it in His mind, as if from the outside, before it was created, and we do not know its rule, because we live inside it, having found it already made.

Brother William of Baskerville

Overview

Attempts to estimate mantle composition fall into two broad categories.

Cosmochemical approaches take meteorites as the basic building blocks; these materials are processed or mixed in order to satisfy such constraints as core size, heat flow and crustal ratios of certain elements. These models constrain the bulk chemistry of the Earth rather than that of the mantle alone. The only primitive meteorites that match satisfactorily both the stable isotope and redox characteristics of the Earth are the enstatite chondrites. The actual material forming the Earth is unlikely to be represented by a single meteorite class. It may be a mixture of various kinds of meteorites and the composition may have changed with time. The oxidation state of accreting material may also have changed with time.

Petrological models take the present continental crust, basalts and peridotites as the basic building blocks. Since basalts represent melts, and peridotites are thought to be residues, some mixture of these should approximate the composition of the upper mantle. Peridotites are the main mantle reservoirs for elements such as magnesium, chromium, cobalt, nickel, osmium and iridium. The continental crust is an important reservoir of the crustal elements; potassium, rubidium, barium, lanthanum, uranium and thorium. Enriched magmas, such as kimberlites, are rare but they are so enriched in the crustal elements that they cannot be ignored. Thus, each of these components plays an essential role in determining the overall chemistry of the primitive mantle. An alternate approach is to search for the most 'primitive' ultramafic rock or component and attribute its composition to the whole mantle or the original mantle, or to take the most depleted MORB and attribute its source region to the whole upper mantle.

The earliest, and simplest, petrological models tended to view the mantle or the upper mantle as homogenous, and capable of providing primitive basalts by partial melting. When the petrological data are combined with isotopic and geophysical data, and with considerations from accretional calculations, a more complex multi-stage evolution is required. Similarly, simple evolutionary models have been constructed from isotope data alone that conflict with the broader database. There is no conflict between cosmochemical, geochemical, petrological and geophysical data, but

a large conflict between models that have been constructed by specialists in these separate fields. The mantle is heterogenous on all scales and there are vast regions of the Earth that are unsampled today because they were isolated by gravitational stratification during accretion of the planet.

The composition of the crust and the upper mantle are the results of a series of melting and fractionation events, including the high-temperature accretion of the planet. Attempts to estimate upper-mantle chemistry usually start from the assumption that it initially was the same as bulk silicate Earth (BSE) and differs from it only by the extraction of the crust, or that the most depleted midocean-ridge basalts (MORB) plus their refractory residues constitute the entire upper mantle. Traditionally, geochemists have assumed that the lower mantle is still undifferentiated BSE. On the other hand, large-scale melting and differentiation upon accretion probably pre-enriched the upper mantle with incompatible elements, including the radioactive elements; the crust and the various enriched and depleted components sampled by current melting events were probably already in the upper mantle shortly after accretion and solidification.

Midocean-ridge basalts represent large degrees of melting of a large source volume, and blending of magmas having different melting histories. The central limit theorem explains many of the differences between MORB and other kinds of melts that sample smaller volumes of the heterogenous mantle. Observed isotopic arrays and mixing curves of basalts, including ocean-island basalts (OIB), can be generated by various stages of melting, mixing, melt extraction, depletion and enrichment and do not require the involvement of unfractionated, primitive or lower, mantle components. However, the first stage in building an Earth – the accretional stage – does involve large degrees of melting that essentially imparted an unfractionated – but enriched – chondritic REE pattern to the upper mantle. Small-degree melts from this then serve to fractionate LIL. Mass-balance and box-model calculations can go just so far in constraining the chemistry of the mantle. Geophysics provides information about physical properties and boundaries in the mantle.

Recycling of crust into the upper mantle is an important process. It is possible to estimate the composition of the fertile upper mantle by combining known components of the upper mantle – basalts, peridotites, recycled crust and so on – in such a way as to satisfy cosmic ratios of the lithophile refractory elements. Other elements are not necessarily concentrated into the crust and upper mantle. The MORB source is just part of the upper mantle and it is not the only LIL depleted part of the mantle. It is not necessarily convectively homogenized.

Attempts to establish an average composition for the upper mantle have focused on MORB because of the assumption the whole upper mantle is the MORB-reservoir. This procedure involves major assumptions about melt generation, melt transport and differentiation processes that have affected these melts, and the sources of non-MORB melts. The depleted upper mantle, that part of the mantle that is assumed to provide MORB by partial melting is variously called DUM, DM, DMM and the convecting upper mantle. Simplified mass balance calculations suggested to early workers that this depleted mantle constituted ~30% of the mantle; the 650–670-km discontinuity was adopted as the boundary between DUM and 'the primitive undepleted undegassed lower mantle'. The starting condition for the upper mantle (UM) was taken as identical to primitive mantle (PM) and the present lower mantle (LM). There are many estimates of PM and BSE based on various cosmological and petrological considerations. The primitive upper mantle – crust plus DUM – is labeled PUM. It was further assumed that the upper mantle was vigorously convecting, well-stirred and chemically homogenous, and extended from the base of the plate to 650-km depth. Thus, this part of the mantle was also called the *convecting mantle*. The non-MORB basalts that occur at the initiation of spreading and at various locations along the global spreading system were attributed to plumes from the lower mantle.

Most or all of the mantle needs to be depleted and degassed to form the crust and upper mantle

and the ^{40}Ar in the atmosphere (e.g. the first edition of Theory of the Earth, or TOE). Depletion of the upper mantle alone cannot explain the continental crust (CC); the MORB reservoir and the CC are not exactly complementary. There must be other components and processes beyond single-stage small-degree melt removal from part of the primordial mantle to form CC. There are other enriched components in the mantle, probably in the shallow mantle. Other depleted components or reservoirs, in addition to the MORB-source, are required by mass-balance calculations. The upper mantle cannot be treated as if its composition can be uniquely determined from the properties of depleted MORB – NMORB or DMORB – and depleted peridotites, continental crust, and an undifferential starting condition.

Both the cosmochemical and petrological approaches utilize terrestrial and meteoritic data. The common theme is that the Earth should have an unfractionated chondritic pattern of the refractory elements. This can be used as a formal a priori constraint in geochemical modeling of the composition of the Earth. This mass balance approach is consistent with the idea that most of the radioactive elements, and other crustal elements, are in the crust and upper mantle. Some investigators, however, decouple their models of the Earth from meteorite compositions. Two extreme positions have been taken: (1) the Earth is a unique body and is not related to material currently in the solar system; upper mantle rocks are representative of the whole mantle and Earth-forming material is not to be found in our meteorite collections; (2) only part of the Earth has been sampled and the upper mantle is not representative of the whole mantle. There are several variants of the second option: (1) the mantle is extensively differentiated and the deepest layers are the dense residues of this differentiation, which is irreversible; (2) only the upper mantle has been processed and differentiated; the deeper mantle is 'primordial'. There are numerous petrological reasons why the Earth's upper mantle should be distinct from any known type of meteorite and why no part of the mantle should have survived in a homogenous primitive state. However, some argue that it is more reasonable that the Earth accreted from material with major-element compositions that were distinct from primitive meteorite types than to accept chemical stratification and petrological differentiation of the mantle.

'Primitive mantle' or PM is the silicate fraction of the Earth, prior to differentiation and removal of the crust and any other parts of the present mantle that are the result of differentiation, or separation, processes. This is called bulk silicate Earth (BSE). In geochemical models, which were popular until very recently, it was assumed that large parts of the Earth escaped partial melting, or melt removal, and are therefore still 'primitive'. Some petrological models assumed that melts being delivered to the Earth's surface are samples from previously unprocessed material. It is difficult to believe that any part of the Earth could have escaped processing during the high-temperature accretional process. 'Primitive mantle', as used here, is a hypothetical material that is the sum of the present crust and mantle. Some petrological models assume that it is a mixture of the MORB-source and continental crust. 'Primitive magma' is a hypothetical magma, the parent of other magmas, which formed by a single-stage melting process of a parent rock and has not been affected by loss of material (crystal fractionation) prior to sampling. It is much more likely that magmas are the result of a multi-stage process and that they represent blends of a variety of melts from various depths and lithologies.

Petrological building blocks

Most mantle magmas can be matched by mixtures of depleted MORB (DMORB) and enriched components (Q). Midocean-ridge basalt (MORB) represents the most uniform and voluminous magma type and is often taken as an end-member for large-ion lithophile (LIL) concentrations and isotopic ratios in other basalts. The uniformity of MORB, however, may be the result of sampling, and the central limit theorem. In this case, MORB is a good average, but not a good end-member. The MORB source has been depleted by removal of a component – Q – that must be rich in LIL

but relatively poor in Na, Al and Ca. Kimberlitic and some other enriched magmas have a complementary relationship to MORB.

The extreme enrichments of kimberlitic magmas in incompatible elements are usually attributed to low degrees of melting and/or metasomatized source compositions. The observed enrichment of kimberlitic magmas with rare earth elements (REE) can be explained in terms of melt migration through source rocks having the composition of normal mantle. The resulting saturated REE spectrum is practically independent of source mineral composition, which may explain the similarity of kimberlites from different geographic localities. Kimberlite is thus an important mantle component and can be used as such – component Q – in mass-balance calculations.

Chemical composition of the mantle

Considerations from cosmochemistry and the study of meteorites permit us to place only very broad bounds on the chemistry of the Earth's interior. These tell us little about the distribution of elements in the planet. Seismic data tell us a little more about the distribution of the major elements. General considerations suggest that the denser major elements will be toward the center of the planet and the lighter major elements, or those that readily enter melts or form light minerals, will be concentrated toward the surface. To proceed further we need detailed chemical information about crustal and mantle rocks. The bulk of the material emerging from the mantle is in the form of melts, or magmas. It is therefore important to understand the chemistry and tectonic setting of the various kinds of magmatic rocks and the kinds of sources they may have come from.

Midocean-ridge basalt represents the most uniform and voluminous magma type and is an end member for LIL concentrations and many isotopic ratios. This is usually taken as one of the *components* of the mantle, even though it itself is an average or a blend. Most mantle magma compositions can be approximated with a mixture of a depleted MORB-component and one or more enriched components, variously called EM1, EM2, HIMU, DUPAL and Q. The resulting magmas themselves are called NMORB, EMORB, OIB, AOB, CFB and so on. The refractory residue left after melt extraction – the *restite* – is usually considered to be a peridotite, dunite or harzburgite, all *ultramafic rocks* (UMR). All of the above, plus *continental crust* (CC), are candidate components for primitive mantle.

Table 13.1 Estimates of average composition of the mantle

Oxide	(1)	(2)	(3)	(4)	(5)
SiO_2	45.23	47.9	44.58	47.3	45.1
Al_2O_3	4.19	3.9	2.43	4.1	3.9
MgO	38.39	34.1	41.18	37.9	38.1
CaO	3.36	3.2	2.08	2.8	3.1
FeO	7.82	8.9	8.27	6.8	7.9
TiO_2	—	0.20	0.15	0.2	0.2
Cr_2O_3	—	0.9	0.41	0.2	0.3
Na_2O	—	0.25	0.34	0.5	0.4
K_2O	—	—	0.11	0.2	(0.13)

(1) Jacobsen and others (1984): extrapolation of ultramafic and chondritic trends.
(2) Morgan and Anders (1980): cosmochemical model.
(3) Maaløe and Steel (1980): extrapolation of lherzolite trend.
(4) 20 percent eclogite, 80 percent garnet lherzolite (Anderson, 1980).
(5) Ringwood and Kesson (1976, Table 7): pyrolite adjusted to have chondritic CaO/Al_2O_3 ratio and Ringwood (1966) for K_2O.

The MORB source appears to have been depleted by removal of a component that is rich in LIL but relatively poor in Na and the clinopyroxene-compatible elements (such as Al, Ca, Yb, Lu and Sc). Kimberlitic magmas have the required complementary relationship to MORB, and I adopt them in the following as a possible Q component. Some elements, such Nb, Ta, Ti and Zr are extraordinarily concentrated into specific minerals – rutile and zircon, for example – and estimates of these elements in rocks can be highly variable and dependent on the amount of these minerals. Peridotites and sulfides are the main carriers of elements such as magnesium,

chromium, cobalt, nickel, osmium and iridium, some of the so-called compatible elements. The continental crust is an important reservoir of potassium, rubidium, barium, lanthanum, uranium and thorium, some of the classical LIL elements. Thus, each of these components plays an essential role in determining the overall chemistry of the primitive mantle.

It is conventional to adopt a single hypothetical mix – lherzolite or harzburgite plus basalt – as the dominant silicate portion of the mantle; this has been called *pyrolite*, for *pyroxene–olivine rock*. An orthopyroxene-rich component (OPX) is also present in the mantle and is required if such major-element ratios as Mg/Si and Al/Ca ratios of the Earth are to be chondritic. Clinopyroxenites, rather than fertile peridotites, may be important source rocks for basalts. Some peridotites appear to have been enriched (metasomatized) by a kimberlite-like (Q) component. Seawater is an important repository of Cl, I and Br. The atmosphere may contain most of the heavier rare gases. Mixtures of the above components, plus continental crust, can be expected to give a first approximation to the composition of primitive mantle.

There may also be inaccessible reservoirs that do not provide samples for us to measure. The so-called missing element and isotope paradoxes in geochemical box-models suggest that some material is hidden away, probably in deep dense layers that formed during the accretion of the Earth. Ratios such as Ca/Al, Mg/Si, U/Pb and U/Nb and some isotope ratios imply that there is hidden or inaccessible material. The most obvious missing elements are iron and other siderophiles, such as Os and Ir. These are in the core. The missing silicon is probably in the perovskite-rich lower mantle. Other missing elements are S and C and other volatiles that left the Earth entirely or were never incorporated into it. There are numerous paradoxes associated with U and Th and their products – heat, Pb-isotopes, He-isotopes and Ne-isotopes. The obvious implication is that we are missing something; the mantle may be chemically stratified and we are sampling only the outer reaches, or we are ignoring certain components such as fluid-filled or melt inclusions, carbonatites and exotic minerals such as rutile, osmiridium etc. It is possible that certain rock types such as lower-crustal cumulates, carbonatites, recycled material and island-arc basalts are not added into the mix in appropriate quantities.

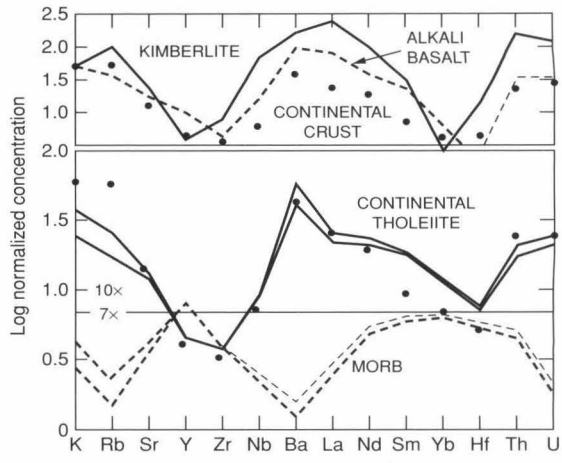

Fig. 13.1 Trace-element concentrations in the continental crust (dots), continental basalts and midocean-ridge basalts (MORB), normalized to average mantle compositions derived from a chondritic model. Note the complementary relationship between depleted basalts (MORB) and the other materials. MORB and continental tholeiites are approximately symmetric about a composition of 7 × C1. This suggests that about 14% of the Earth may be basalt. For other estimates, see text.

Figure 13.1 shows representative compositions of kimberlite, crust, MORB and ultramafic rock. For many refractory elements kimberlite and crust have a similar enrichment pattern. However, the volatile/refractory ratios are quite different, as are ratios involving strontium, hafnium, titanium, lithium, yttrium, ytterbium and lutetium. Kimberlite and MORB patterns are nearly mirror images for the refractory elements, but this is only approximately true for MORB and crust, especially for the HREE, and the small-ion–high-charge elements. MORB and kimberlite also represent extremes in their strontium and neodymium isotope compositions.

When LIL-rich materials (KIMB, lamproites) are mixed with a depleted magma (MORB), the resulting blend can have apparently paradoxical geochemical properties. For example, the hybrid

magma can have such high La/Yb, Rb/Sr and Pb-isotope ratios that derivation from an enriched source is indicated, but the Sr- and Nd-isotope ratios imply derivation from an ancient depleted reservoir. Many island, island-arc and continental basalts have these characteristics. These apparently paradoxical results simply mean that ratios do not average as do concentrations. An additional complication is that the melt components, and the mixed hybrid, can experience crystal fractionation while mixing. Magma mixtures and evolved magmas do not necessarily define simple mixing lines.

The isotope zoo

A large number of components in MORB and OIB have been proposed and labeled. These are primarily based on isotopic characteristics. A short list is: EM1, EM2, HIMU, DUPAL, C, PHEM, PREMA, FOZO, LOMU, LONU and Q. The origin of the isotope species in the mantle zoo is a matter of considerable controversy. In the isotope geochemistry literature these are attributed to the lower mantle and to plumes but there is no evidence that this is the case. There is considerable evidence that all these species originated at the surface of the Earth, in the crust or in the lithosphere, and may have evolved in the shallow mantle. Various kinds of altered and recycled materials have been proposed as contributors or ancestors to these species. Among the suggestions are oceanic sediments, recycled oceanic crust with some pelagic sediments (EM1), continental sediments or dehydrated oceanic sediments (EM2), altered oceanic crust and sediments or ancient altered MORB (HIMU), delaminated lower continental crust (EM1, DUPAL), peridotites, and high ^{3}He/U and low U and Th bubbles in depleted lithosphere, restites or cumulates (FOZO). Some EM components of the mantle have oxygen isotopic compositions similar to MORB and peridotite xenoliths, ruling out a large contribution of subducted sediment and other sources that were proposed on the basis of Sr and Nd isotopes alone.

All of these species may co-exist in the shallow mantle, along with the sources of MORB; they do not have to be recycled into the deep lower mantle before they return to the surface. Observed magmas are blends or mixtures of components, or partial melts therefrom, with various isotopic signatures followed by variable degrees of crystal fractionation and reactions with the crust and mantle on the way to the surface. Trace-element and isotope ratios of mixtures can have anti-intuitive properties.

The recipes and mathematics of mixtures

Rocks, and the mantle, are composed of *components*. Let us call them A, B, C . . . The fraction of each component in the mix is x, y, z . . . The mixture itself, M, has properties that are the appropriate weighted average of the properties of the components. It is straightforward to construct a rock, or a mantle, or a fruitcake, if we know all the ingredients and the proportions in which they occur. It is not straightforward to infer the ingredients and the mixing ratios if we just have samples from M, or if we know the ingredients but not the proportions. Our inferences depend on assumptions and how we sample M. There are techniques, known as geophysical inverse theory, sampling theory and the central limit theorem (CLT) for approaching these kinds of problems.

Consider first, the fruitcake. The *components* are bits of fruit and dough. Every large bite is more-or-less the same. Every tiny bite is different, a different bit of fruit or a different combination. The big bites have very little variance in composition or taste, while the compositions (tastes) of the small bites have enormous scatter. This is a consequence of the CLT. One cannot infer the composition of the fruitcake from the homogenous big bites, one can only infer the average taste.

Consider next, the rock. A rock is composed of minerals, inclusions and intergranular material. By grinding up a large sample, one infers the average composition of the rock. Many such samples from a homogenous outcrop will give similar results. That is, there will be little scatter or variance. However, if very small samples are taken, there will be enormous variance, a reflection of

the basic heterogeneity of rocks. However, the mean of all the small samples will be close to the means of the large samples. This is another consequence of the CLT. The homogeneity of the large samples does not mean that the rock is homogenous; it simply means that large-scale, large-volume averages have been taken. Multiple microprobe analyses of the same rock would tell a different story. Some small-scale samples would give extreme compositions, compositions not evident in any of the large-volume averages. This does not mean that they come from a different rock.

Finally, consider the mantle. We have homogenous samples of MORB from midocean ridges, which are enormous blending and averaging machines. Seamounts on the flanks of oceanic ridges provide smaller volume samples from the same mantle, and these exhibit enormous variance. Ocean-island basalts also exhibit a wide range of compositions, partly a reflection of the large-scale heterogeneity of the mantle and partly a reflection of the nature and scale of the sampling process. Sometimes the magmas bring up small fragments, or xenoliths, from the mantle. These are highly variable in composition and sometimes exhibit a greater range of compositions than one observes globally in basalts. Midocean-ridge basalts are blends of magmas and solid materials from huge volumes, and, as expected, they show little variance, at least in some properties. MORB is not a *component* or a *reservoir*; it is an average, and will be treated as such below.

Considering all of this, how does one infer the composition of the mantle? One approach is to assume that one knows the composition and volume of the major reservoirs such as the crust and the upper mantle and then to attribute discrepancies to the lower mantle or other hidden reservoirs. The pyrolite model assumes that the mantle is composed of known amounts and compositions of a mafic and an ultramafic component. A more objective approach is to make a list of all the materials that are known to enter and leave the mantle and construct a composite from these that satisfies certain constraints. These constraints might include the total volume of the crust (one of the components), the sum of the components is 1, and the ratios of some of the components should be chondritic. This is the approach taken in the following. It is clearly important to know something about the various components; magmas, ultramafic rocks, crust, kimberlites and so on. Most of the components are also mixtures of other components. In some cases, and for some elements, it may be important to consider mineral components, such as zircon and rutile, or rare magmas such as carbonatites. The reason for this is the same reason that one must include the crust in any mass balance in spite of the fact that it has a very small total volume. Some rocks have concentrations of some elements that exceed the crustal concentrations by an order of magnitude; one cannot ignore such rocks. For a complete mass balance one cannot even ignore the oceans and the atmosphere; iodine and chlorine, for example, are concentrated on the atmosphere and the biosphere.

In addition to all the above, one must always remember that isotopic and trace-element ratios do not average and mix as do concentrations or absolute abundances.

The inverse approach

The inverse approach is more widely used in geophysics than in geochemistry. The problem is one of inferring mantle chemistry from various products of differentiation, which themselves are averages. One alternative approach is to use petrological insight to pick the most representative constituents for the mantle, and to adjust their proportions to satisfy certain key constraints or assumptions.

The refractory elements can be assumed to be in the Earth in chondritic ratios but we do not know the absolute concentrations or their distribution. In order to estimate absolute concentrations, and the volatile and siderophile content of the mantle, we seek a linear combination of components that gives chondritic ratios for the refractory elements. We can then estimate such key ratios as Rb/Sr, K/U and U/Pb that involve nonrefractory elements. In essence, we replace the five basic building blocks of mantle chemistry, ol,

Table 13.2 | Chemical composition of mantle components (ppm, % or ppb).

	MORB	Ultramafic Rocks	KIMB	Crust	Picrite	OPX	Morgan and Anders (1980)
Li	9	1.5	25	10	7	1.5	1.85
F	289	7	1900	625	219	—	14
Na	15 900	2420	2030	26 000	12 530	—	1250
Mg*	5.89	23.10	16.00	2.11	10.19	21.00	13.90
Al*	8.48	2.00	1.89	9.50	6.86	1.21	1.41
Si*	23.20	21.80	14.70	27.10	22.85	22.60	15.12
P	390	61	3880	1050	308	—	1920
S	600	8	2000	260	452	—	14 600
Cl	23	1	300	1074	17	—	20
K	660	35	17 600	12 500	504	10	135
Ca*	8.48	2.40	7.04	5.36	6.96	1.32	1.54
Sc	37.3	17	15	30	32	12	9.6
Ti	5500	1000	11 800	4800	4375	800	820
V	210	77	120	175	177	60	82
Cr	441	2500	1100	55	956	2500	4120
Mn	1080	1010	1160	1100	1063	1010	750
Fe*	6.52	6.08	7.16	5.83	6.41	6.08	32.07
Co	53	105	77	25	66	105	840
Ni	152	2110	1050	20	642	2110	18 200
Cu	77	15	80	60	62	30	31
Zn	74	60	80	52	71	20	74
Ga	18	4	10	18	14	3	3
Ge	1.5	1.1	0.5	1.5	1.4	1.1	7.6
Se	0.181	0.02	0.15	0.05	0.14	0.006	9.6
Rb	0.36	0.12	65	42	0.30	0.04	0.458
Sr	110	8.9	707	400	85	4.5	11.6
Y	23	4.6	22	22	18	0.023	2.62
Zr	70	11	250	100	55	5.5	7.2
Nb	3.3	0.9	110	11	2.7	0.45	0.5
Ag	0.019	0.0025	—	0.07	0.015	0.001	0.044
Cd	0.129	0.255	0.07	0.2	0.103	0.01	0.016
In	0.072	0.002	0.1	0.1	0.055	—	0.002
Sn	1.36	0.52	15	2	1.15	0.52	0.39
Cs	0.007	0.006	2.3	1.7	0.01	0.002	0.0153
Ba	5	3	1000	350	4.50	2	4
La	1.38	0.57	150	19	1.18	0.044	0.379
Ce	5.2	1.71	200	38	4.33	0.096	1.01
Nd	5.61	1.31	85	16	4.54	0.036	0.69
Sm	2.08	0.43	13	3.7	1.67	0.009	0.2275
Eu	0.81	0.19	3	1.1	0.66	0.0017	0.079
Tb	0.52	0.14	1	0.64	0.43	0.0017	0.054
Yb	2.11	0.46	1.2	2.2	1.70	0.0198	0.229
Lu	0.34	0.079	0.16	0.03	0.27	0.0072	0.039
Hf	1.4	0.34	7	3	1.14	0.17	0.23

(cont.)

Table 13.2 | *(cont.)*

	MORB	Ultramafic Rocks	KIMB	Crust	Picrite	OPX	Morgan and Anders (1980)
Ta	0.1	0.03	9	2	0.08	—	0.023
Re†	1.1	0.23	1	1	0.88	0.08	60
Os†	0.04	3.1	3.5	5	0.81	3.1	880
Ir†	0.0011	3.2	7	1	0.80	3.2	840
Au†	0.34	0.49	4	4	0.38	0.49	257
Tl†	0.01	0.02	0.22	0.25	0.01	—	0.00386
Pb	0.08	0.2	10	7	0.11	—	0.068
Bi	0.007	0.005	0.03	0.2	0.01	—	0.00294
Th	0.035	0.094	16	4.8	0.05	—	0.0541
U	0.014	0.026	3.1	1.25	0.02	—	0.0135

*Results in percent.
†Results in ppb.
Anderson (1983a).

opx, cpx, gt and Q, or their low-pressure equivalents) with four composites or averages; peridotite, orthopyroxenite, basalt and Q. In practice, we can use two different ultramafic rocks (UMR and OPX) with different ol/opx ratios to decouple the ol+opx contributions. The chemistry of the components (MORB, UMR, OPX and crust) are given in Table 13.2.

Having measurements of m elements in n components where m far exceeds n, we can find the weight fraction x_j of each component, given the concentration C_j of the jth element in the ith component, that yields chondritic ratios of the refractory oxyphile elements. In matrix form,

$$C_{ij}x_j = kC_j \tag{1}$$

where C_j is the chondritic abundance of element j and k is a dilution or enrichment factor, which is also to be determined. The least-squares solution is

$$x_j/k = (C^{\mathrm{T}}C)^{-1}C^{\mathrm{T}}C_j \tag{2}$$

where C^{T} is the matrix transpose of C, with the constraints

$$\sum x_i = 1 \text{ and } k = \text{constant} \tag{3}$$

Equation 1 then gives the mantle concentrations of the volatile and siderophile elements, elements not used in the inversion.

Schematically, primitive mantle can be written

$$\mathrm{PM} = \mathrm{MORB} + \mathrm{UMR} + \mathrm{CC} + \mathrm{OPX} + \mathrm{Q}$$

and the proportions of each component are found by the inversion.

The mixing ratios found from Equations 2 and 3 are UMR, 32.6%, OPX, 59.8%, MORB, 6.7%, crust, 0.555% and Q, 0.11%. This is a model composition for primitive mantle (PM) i.e. mantle plus crust. The Q component is equivalent to a global layer 3.6 km thick. The MORB component represents about 25% of the upper mantle. This solution is based on 18 refractory elements and, relative to chondrite (C1) abundances, yields k = 1.46.

The result is given in Table 13.3 under 'mantle plus crust.' This will be referred to as the bulk silicate Earth (BSE) composition. Concentrations normalized to Cl are also given. Note that the high-charge, small-ionic radius elements (Sc, Ti, Nb and Hf) have the highest normalized ratios and may be overestimated. Taking all the refractory oxyphile elements into account (23 elements), the normalized enrichment of the refractory elements in the mantle plus crust is 1.59. If five elements (Fe, S, Ni, Co and O) are removed from C1 to a core of appropriate size and density, the remaining silicate fraction will be enriched

Table 13.3 | Chemical composition of mantle (ppm, % or ppb)

	CI	Morgan and Anders (1980)	UDS	Upper Mantle	Lower Mantle	Mantle + Crust	Normalized to Morgan and Anders (1980)	Normalized to CI
Li	2.4	1.85	7.48	3.49	1.50	2.09	0.76	0.87
F	90	14	259	91	1	28	1.39	0.31
Na	7900	1250	13 172	6004	359	2040	1.10	0.26
Mg*	14.10	13.90	9.80	18.67	21.31	20.52	1.00	1.46
Al*	1.29	1.41	6.95	3.65	1.33	2.02	0.97	1.57
Si*	15.60	15.12	23.00	22.20	22.48	22.40	1.00	1.44
P	1100	1920	387	170	9.06	57	0.02	0.05
S	19 300	14 600	458	158	1.19	48	0.0022	0.0025
Cl	1000	20	79	27	0.07	8	0.27	0.008
K	890	135	1356	475	14	151	0.76	0.17
Ca*	1.39	1.54	6.87	3.89	1.48	2.20	0.96	1.58
Sc	7.8	9.6	31.92	22	13	15	1.09	1.99
Ti	660	820	4477	2159	830	1225	1.01	1.86
V	62	82	176	110	63	77	0.63	1.24
Cr	3500	4120	907	1969	2500	2342	0.38	0.67
Mn	2700	750	1066	1029	1010	1016	0.91	0.38
Fe*	27.20	32.07	6.39	6.18	6.08	6.11	0.13	0.22
Co	765	840	64	91	105	101	0.08	0.13
Ni	15 100	18 200	611	1610	2110	1961	0.07	0.13
Cu	160	31	62	31	28	29	0.62	0.18
Zn	455	74	70	63	26	37	0.34	0.08
Ga	14	3	15	7	3	4	0.94	0.31
Ge	47	7.6	1.40	1.20	1.10	1.13	0.10	0.02
Se	29	9.6	0.14	0.06	0.01	0.02	0.0016	0.0008
Rb	3.45	0.458	3.32	1.19	0.05	0.39	0.57	0.11
Sr	11.4	11.6	109	42.3	5.2	16.2	0.94	1.42
Y	2.1	2.62	18.64	9.28	0.70	3.26	0.84	1.55
Zr	5.7	7.2	60	27	6	13	1.18	2.20
Nb	0.45	0.5	4.30	2.03	0.52	0.97	1.31	2.15
Ag	0.27	0.044	0.02	0.01	0.00	0.003	0.05	0.01
Cd	0.96	0.016	0.11	0.05	0.01	0.02	1.03	0.03
In	0.12	0.002	0.06	0.02	0.0003	0.006	2.13	0.05
Sn	2.46	0.39	1.34	0.79	0.52	0.60	1.04	0.24
Cs	0.29	0.0153	0.13	0.05	0.003	0.02	0.68	0.05
Ba	3.60	4	34	13	1.72	5.22	0.88	1.45
La	0.367	0.379	3.75	1.63	0.12	0.57	1.02	1.56
Ce	0.957	1.01	8.28	3.90	0.34	1.40	0.93	1.46
Nd	0.711	0.69	6.03	2.88	0.23	1.02	1.00	1.43
Sm	0.231	0.2275	1.90	0.92	0.07	0.32	0.96	1.40
Eu	0.087	0.079	0.70	0.362	0.03	0.13	1.10	1.48
Tb	0.058	0.054	0.44	0.241	0.02	0.09	1.09	1.51
Yb	0.248	0.229	1.72	0.88	0.09	0.32	0.95	1.30
Lu	0.038	0.039	0.27	0.144	0.02	0.06	0.96	1.46
Hf	0.17	0.23	1.30	0.66	0.20	0.33	0.98	1.96

(cont.)

Table 13.3 | (*cont.*)

	CI	Morgan and Anders (1980)	UDS	Upper Mantle	Lower Mantle	Mantle + Crust	Normalized to Morgan and Anders (1980)	Normalized to CI
Ta	0.03	0.023	0.28	0.11	0.004	0.04	1.10	1.24
Re†	60	60	0.89	0.45	0.10	0.21	0.0023	0.0034
Os†	945	880	1.08	2.43	3.10	2.90	0.0022	0.0031
Ir†	975	840	0.88	2.43	3.20	2.97	0.0024	0.0031
Au†	255	257	0.62	0.53	0.49	0.50	0.0013	0.002
Tl†	0.22	0.0039	0.03	0.02	0.00	0.01	1.28	0.033
Pb	3.6	0.068	0.60	0.33	0.03	0.12	1.19	0.033
Bi	0.17	0.0029	0.02	0.009	0.0007	0.0033	0.75	0.019
Th	0.051	0.0541	0.48	0.224	0.014	0.0765	0.96	1.50
U	0.014	0.0135	0.12	0.057	0.004	0.0196	0.98	1.40

*Results in percent.
†Results in ppb.
Anderson (1983a).

in the oxyphile elements by a factor of 1.48. This factor matches the value for k determined from the inversions.

The Earth's mantle can be chondritic in major and refractory-element chemistry if an appreciable amount of oxygen has entered the core. H_2O and CO_2 are not included in most mass balance calculations and unknown amounts of these may be in the upper mantle or escaped from the Earth.

Table 13.3 compares these results with cosmochemically based models. Both the volatile elements and the siderophile elements are strongly depleted in the crust–mantle system relative to cosmic abundances.

In pyrolite-type models, it is assumed that primitive mantle (PM) is a mix of basalt and peridotite and that one knows the average compositions of the basaltic (MORB or OIB) and ultramafic (UMR) components. These are mixed in somewhat arbitrary, predetermined, proportions; the results are comparable with volatile-free chondritic abundances for some of the major elements.

Tholeiitic basalts are thought to represent the largest degree of partial melting among common basalt types and to nearly reflect the trace-element chemistry of their mantle source. Tholeiites, however, range in composition from depleted midocean-ridge basalts to enriched ocean-island basalts (OIB) and continental flood basalts (CFB). Enriched basalts (alkali-olivine, OIB, CFB) can be modeled as mixtures of MORB and an enriched (Q) component that experience varying degrees of crystal fractionation prior to eruption. Ultramafic rocks from the mantle, likewise, have a large compositional range. Some appear to be crystalline residues after basalt extraction, some appear to be cumulates, and others appear to have been secondarily enriched in incompatible elements (metasomatized). This enriched component is similar to the Q component of basalts. Some ultramafic rocks are relatively 'fertile' (they can yield basalts upon partial melting), but they do not have chondritic ratios of all the refractory elements.

The above calculation, in essence, decomposes the basaltic component of the mantle into a depleted (MORB) and LIL-enriched (Q) component. These can be combined and compared with the basaltic component of other two-component models, such as pyrolite, by comparing 'undepleted basalt' (MORB +1.5% KIMB) with the basalts (Hawaiian tholeiite or 'primitive' oceanic tholeiite) used in the construction of pyrolite. The present model has an undepleted basaltic component (MORB + Q) of 914 ppm

potassium, 0.06 ppm uranium and 0.27 ppm thorium. The basaltic components of pyrolite have much higher concentrations of these and other LIL. Refractory ratios such as U/Ca and Th/Ca for pyrolite are about 50% higher than chondritic because of the high LIL content of the arbitrarily chosen basalt. One disadvantage of two-component pyrolite-type models is that the final results are controlled by the arbitrary choice of components, including basalt, and compositions. Indeed, the various pyrolite models differ by an order of magnitude in, for example, the abundance of potassium.

By and large, there is excellent agreement with cosmochemical models (Table 13.3) and BSE found by the above inversion. In the present model, the alkalis lithium, potassium, rubidium and cesium are somewhat more depleted than in M&A, as are volatiles such as chlorine, vanadium and cadmium. The Rb/Sr and K/U ratios are correspondingly reduced. The elements that are excessively depleted (P, S, Fe, Co, Ni, Ge, Se, Ag, Re, Os, Ir and Au) are plausibly interpreted as residing in the core. Note that the chalcophiles are not all depleted. In particular, lead is not depleted relative to other volatiles such as manganese, fluorine and chlorine, which are unlikely to be concentrated in the core. The composition of primitive mantle, derived by the above approach, is given in Figure 13.2.

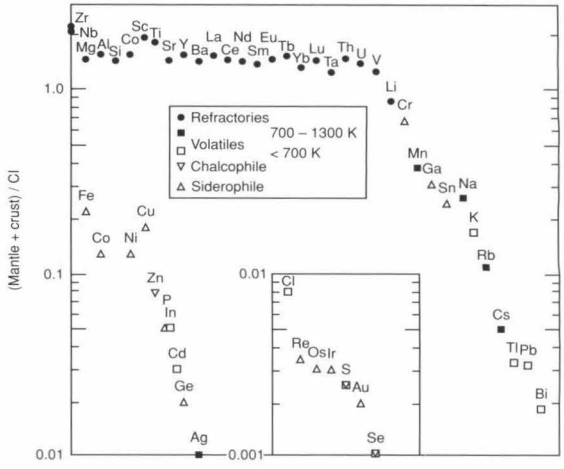

Fig. 13.2 Abundances of elements in 'primitive mantle' (mantle + crust) relative to CI, derived by mixing mantle components to obtain chondritic ratios of the refractory lithophile elements.

Some elements are extraordinarily concentrated into the crust. The above results give the following proportions of the total mantle-plus-crust inventory in the continental crust; rubidium, 58%; cesium, 53%; potassium, 46%; barium, 37%; thorium and uranium, 35%; bismuth, 34%; lead, 32%; tantalum, 30%; chlorine, 26%; lanthanum, 19% and strontium, 13%.

In addition, the atmospheric ^{40}Ar content represents 77% of the total produced by 151 ppm potassium over the age of the Earth. This has probably degassed from the crust and upper mantle and probably reflects 23% retention, rather than 23% primordial undegassed mantle. These results all point toward an extensively differentiated Earth and efficient upward concentration of the incompatible trace elements. It is difficult to imagine how these concentrations could be achieved if the bulk of the mantle is still primitive or unfractionated. If only the upper mantle provides these elements to the crust, one would require more than 100% removal of most of the LIL (U, Th, Bi, Pb, Ba, Ta, K, Rb and Cs). More likely, the whole mantle has contributed to crustal, and upper-mantle, abundances, and most of the mantle is strongly depleted and, probably, infertile. The crust, MORB reservoir and the Q component account for a large fraction of the incompatible trace elements. It is likely, therefore, that the lower mantle is depleted in these elements, including the heat producers potassium, uranium and thorium.

In an alternative approach we can replace UMR and OPX by their primary constituent minerals, olivine, orthopyroxene and clinopyroxene. The present mantle can then be viewed as a five-component system involving olivine, orthopyroxene, clinopyroxene, MORB (cpx and gt) and Q. In this case the LIL inventory of the primitive mantle is largely contained in four components: MORB, Q, clinopyroxene and CRUST. The results of this approach are: olivine, 33%, orthopyroxene, 48.7%, clinopyroxene, 3.7%, MORB, 14.0%, Q, 0.085% and CRUST, 0.555%.

Concentrations of certain key elements are sodium, 2994 ppm, potassium, 205 ppm,

Table 13.4 Elemental ratios.

	CI	Morgan and Anders*	UDS	Upper Mantle	Lower Mantle	Mantle + Crust	Normalized M & A*	Normalized CI
Rb/Sr	0.3026	0.0395	0.0304	0.0281	0.0101	0.024	0.61	0.08
K/U	63 571	10 000	11 429	8356	3552	7693	0.77	0.12
Sm/Nd	0.3249	0.3297	0.315	0.319	0.318	0.319	0.968	0.982
Th/U	3.64	4.01	4.08	3.94	3.62	3.98	0.97	1.07
U/Pb	0.0039	0.20	0.20	0.17	0.13	0.16	0.82	42
La/Yb	1.48	1.66	2.18	1.85	1.43	1.77	1.07	1.20
K/Na	0.11	0.11	0.10	0.08	0.04	0.07	0.69	0.66
Mg/Si	0.90	0.92	0.43	0.84	0.95	0.92	1.00	1.01
Ca/Al	1.08	1.09	0.99	1.07	1.12	1.09	1.00	1.01
Yb/Sc	0.032	0.024	0.054	0.04	0.007	0.021	0.87	0.65
Ce/Nd	1.35	1.46	1.37	1.35	1.49	1.37	0.94	1.02
Eu/Nd	0.12	0.11	0.12	0.13	0.13	0.13	1.10	1.03
Yb/Lu	6.53	5.87	6.26	6.10	4.77	5.80	0.99	0.89
Sr/Ba	3.17	2.90	3.17	3.14	2.99	3.11	1.07	0.98
U/La	0.038	0.036	0.03	0.035	0.032	0.034	0.97	0.90

*Model of Morgan and Anders (1980).

rubidium, 0.53 ppm, strontium, 25 ppm and cesium, 0.02 ppm. The alkalis are generally within 50% of the concentrations determined previously. The K/U ratio is 44% lower.

A four-component (crust, basalt, peridotite and Q) model for the upper mantle gives close to chondritic ratios for the refractory trace elements. The model gives predictions for volatile/refractory ratios such as K/U and Rb/Sr. It predicts that EMORB in the upper mantle can be up to 10% of NMORB.

For BSE a pyroxene-rich component is required in order to match chondritic ratios of the major elements. Such a component is found in the upper mantle and is implied by the seismic data for the lower mantle. The abundances in the mantle-plus-crust system (BSE) are 151 ppm potassium, 0.0197 ppm uranium and 0.0766 ppm thorium, giving a steady-state heat flow that implies that slightly more than half of the terrestrial heat flow is due to cooling of the Earth, consistent with convection calculations in a stratified Earth.

In summary, primitive mantle (PM) can be viewed as a five-component system; crust, MORB, peridotite, pyroxenite and Q (quintessence, the fifth essence) or, alternatively, as olivine, orthopyroxene, garnet plus clinopyroxene (or basalt) and incompatible element- and alkali-rich material (crust and kimberlite or LIL-rich magmas). Advantages of the inverse method are that the mixing proportions do not have to be fixed in advance and all potential components can be included; the inversion will decide if they are needed.

The upper mantle

The mass-balance method gives the average composition of the mantle but makes no statement about how the components are distributed between regions of the mantle. We can, however, estimate the composition of the MORB source region prior to extraction of crust and Q. The bulk of the mantle is depleted and refractory, UMR plus orthopyroxene (OPX). Pyroxenite, the most uncertain and to some extent arbitrary of the components, plays a minor role in the mass-balance calculations for the trace refractories and is required mainly to obtain chondritic ratios of major elements. Detailed discussion of the composition of the upper mantle is postponed until Chapter 26.

Table 13.5 | Elemental ratios in upper-mantle components

	MORB	Ultramafic Rocks	KIMB	Crust	Picrite	OPX	Morgan and Anders (1980)
Rb/Sr	0.0033	0.0135	0.0919	0.105	0.0035	0.0089	0.039
K/U	47 143	1346	5677	10 000	29 632	—	10 000
Sm/Nd	0.371	0.328	0.153	0.231	0.368	0.25	0.3297
Th/U	2.50	3.62	5.16	3.84	2.94	—	4.01
U/Pb	0.18	0.13	0.31	0.18	0.15	—	0.20
La/Yb	0.65	1.24	125	8.64	0.69	2.22	1.66
K/Na	0.84	0.01	8.67	0.48	0.04	—	0.11
Mg/Si	0.25	1.06	1.09	0.08	0.45	0.93	0.92
Ca/Al	1.00	1.20	3.72	0.56	1.01	1.09	1.09
Yb/Sc	0.057	0.027	0.08	0.073	0.053	0.0017	0.0239
Ce/Nd	0.93	1.31	2.35	2.38	0.95	2.67	1.46
Eu/Nd	0.14	0.15	0.04	0.07	0.14	0.05	0.11
Yb/Lu	6.21	5.82	7.50	7.33	6.18	2.75	5.87
Sr/Ba	22.00	2.97	1.18	1.14	18.83	3.00	2.90
U/La	0.01	0.46	0.021	0.066	0.014	—	0.036

We first find the composition of a possible picritic parent to MORB. The relation PICRITE = 0.75 MORB + 0.25 UMR gives the results tabulated under 'picrite' in Table 13.2 and 13.4.

The mixing ratios that are required to give a chondritic pattern for the refractory elements yield

$$\text{UDS} = 0.935\ \text{PICRITE} + 0.016\ \text{Q} + 0.00559\ \text{CRUST}$$

The composition of this reconstructed *Undepleted Source Region* is tabulated under UDS. This has also been called primitive upper mantle (PUM). UDS accounts for about 10% of the mantle. The remainder of the mantle above 670-km depth is assumed to be ultramafic rocks (UMR). This gives the composition tabulated under 'upper mantle' in Tables 13.3 and 13.4. This region contains 23.4% basalt (MORB). The resulting composition has element ratios (Table 13.5), which, in general, are in agreement with chondritic ratios. The La/Yb, Al/Ca and Si/Mg ratios, however, are too high. These are balanced by the deeper mantle in the full calculation. The solution for the mantle below 670-km depth, is 0.145 UMR and 0.855 OPX. This gives chondritic ratios for Mg/Si and Ca/Al for the Earth as a whole. The mixing

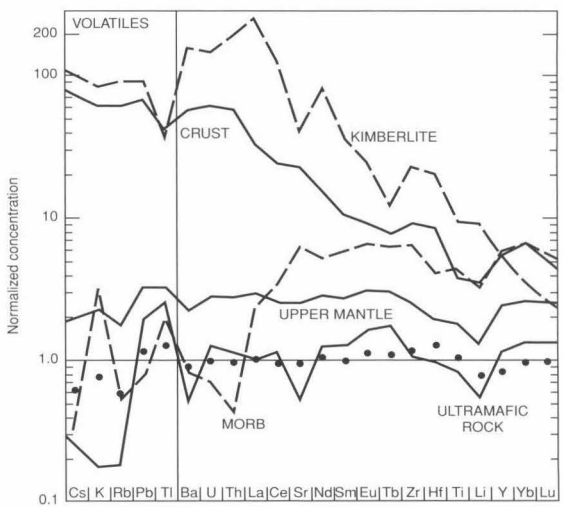

Fig. 13.3 Shows the normalized concentrations of the lithophile elements in the various components, upper mantle and mantle-plus-crust. The refractory elements in the upper mantle have normalized concentrations of about 3; this includes the crustal contribution. Since the upper mantle is about one-third of the whole mantle, a strongly depleted lower mantle is implied. Note that the upper mantle is depleted in lithium and titanium. These elements may be in the inaccessible lower mantle (below 1000 km). The composition of the upper mantle is discussed in more detail in Chapter 23. Dots are derived PM.

ratios will be slightly different if it is assumed that the upper mantle extends to 1000-km depth, which is the classical depth to the top of the lower mantle. An orthopyroxene-rich composition for the bulk of the mantle is expected with a chondritic model for the major elements, particularly if the upper mantle is olivine- and basalt-rich. At low pressure olivine and orthopyroxene are refractory phases and are left behind as basalt is removed. However, at high pressure the orthopyroxene-rich phases, majorite and perovskite, are both refractory and dense. If melting during accretion extended to depths greater than about 350-km, then the melts would be olivine-rich and separation of olivine from orthopyroxene can be expected.

Figure 13.3 shows the concentrations of the lithophile elements in the various components, all normalized to mantle equivalent concentrations. The refractory elements in the upper mantle have normalized concentrations of about 3. Since the upper mantle is about one-third of the whole mantle, a strongly depleted lower mantle is implied. The upper mantle is not necessarily homogenous. The basaltic fraction, as eclogite, may be in a separate layer. Seismic data are consistent with an eclogite-rich transition region.